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Selective solar absorber coatings on receiver tubes for CSP – energy-efficient production process by sol-gel dip-coating and subsequent induction heating

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Abstract

The energy efficiency of production processes for components of solar energy systems is an important issue. Other factors, which are important for the production of black selective solar coatings include production speed, cycle time and homogeneity of the coating, as well as the minimization of the quantity of the needed chemical precursors. In this paper a new energy-efficient low-cost production process is presented for production of optically selective coatings for solar thermal absorbers.

The used method to produce such coatings is sol-gel dip-coating for which all the solutions have been synthetized at the Solar Energy and Building Physics Laboratory of EPFL. The used precursors are tetraethyl orthosilicate, manganese acetate tetrahydrate, copper chloride dihydrate and cobalt chloride hexahydrate. Solutions were obtained by dissolving these precursors in a solution based on a mixture of absolute ethanol, nitric acid and demineralized water.

The layers deposited on sheetlike substrates were annealed in a benchtop furnace. For 2 meter long austenitic stainless steel tubes, a novel, fast and energy-efficient process based on induction heating was developed for the thermal annealing. An induction coil passes along the tube. An alternating current flowing in the coil induces a current in the tube. By resistive heating, the temperature of both the metallic tube wall and the deposited film increases. The homogeneity of the temperature distribution of the tube after a single passage of the coil was monitored by infrared imaging.

The optical and morphological properties of the Cu-Co-Mn-Si-O based triple layer have been characterized by spectrophotometry, transmission electron microscopy (TEM), time-of-flight secondary ion mass spectroscopy (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS). After optimization of the multilayer design, a solar absorptance of 0.95 and a thermal emissivity of 0.12 at 100°C have been achieved. The intermediate Cu-Co-Mn-Si-O layer was analyzed by transmission electron microscopy. The likewise obtained images show an agglomeration of crystalline grains with 5-20 nm in diameter. Therefore, we can consider that the Cu-Co-Mn-Si-O phase is nanocrystalline.

In order to roughly estimate the corrosion resistance of the coating in an acidic environment, a simple corrosion test in harsh conditions confirmed the durability of the novel sol-gel coating. Moreover, the excellent stability at elevated

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temperatures in ambient air makes the coating an interesting candidate for solar applications involving concentrated solar radiation, such as the generation of solar electricity (concentrated solar power), industrial process heating and solar cooling. For that reason, prototype coatings consisting of stacks of three individual layers were deposited on 2 meter long stainless steel tubes.

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Black selective surface; thin films; sol-gel dip-coating; stainless steel; Cu-Co-Mn-Si-O; spectrophotometry; ToF-SIMS; XPS; tube; induction heating; thermal annealing; concentrated solar power (CSP).

1. Introduction

The conversion of solar radiation is considered as a very efficient way to provide space heating, domestic hot water, industrial process heating, desalinated seawater or generation of solar electricity. One key element for all these applications is the optically selective coating on the solar absorber, which should ideally behave as a black body, absorbing a maximum of the incoming solar radiation, while minimizing energy losses by infrared radiation, thus acting as an infrared mirror. Therefore, a selective surface should have the lowest possible spectral reflectivity in the spectral range of solar radiation and the highest possible one in the range of infrared emission at the given temperature of the absorber. For non-concentrated applications below 300°C, a wavelength of approximately 2500 nm can be considered as transition point between these two spectral bands. In nature, no materials exist with perfect intrinsic selective properties.

Different types of selective absorbing surfaces exist, which are described in detail by Agnihotri *et al*. [1]: intrinsic absorbers, absorber-reflector tandems, multilayered interference stacks, optical trapping systems, powdered semiconductor reflector combinations (selective paints), composite material films and quantum-size effect materials. In order to be cost effective, commercially available selective coatings for glazed solar collectors should typically absorb at least 95% of the incoming solar radiation and have a thermal emittance lower than 0.05. Selective coatings for solar thermal collectors are either produced by traditional electrodeposition of black chrome [2, 3], like selective paint [4], or by vacuum deposition processes such as reactive evaporation or magnetron sputtering [5-7]. In the electroplating process, toxic Cr(VI) ions are used and care has to be taken to avoid environmental pollution: despite the fact that this product is very durable, it is problematic due to the environmental impact of the involved precursors. On the other hand, vacuum deposition leads to large front costs because of the expensive equipment required and can be out of reach for potential producers.

This explains the interest in developing a sol-gel process for the production of nanocomposite selective solar absorber coatings. Indeed, sol-gel processing does not require expensive vacuum equipment and allows to completely avoid the use of toxic chrome.

Kaluza *et al*. [8] demonstrated that it is possible to reach a solar absorptance of 0.86 and a thermal emissivity of 0.11 by sol-gel method with a single layer of $CuCoMnO_x$. Using sol-gel spin-coating, Boström *et al*. [9] obtained competitive properties for multilayered coatings with nitrogen annealing: Al_2O_3:Ni multilayered coating absorbs 97% of the incoming solar energy for a thermal emittance lower than 0.05. Recently, Bayón *et al*. [10, 11] obtained highly selective coatings based on Cu-Mn-Si oxides that show excellent optical performance. A solar absorptance of 0.95 combined with a thermal emittance of 0.035 was achieved for coatings on aluminium substrates.

Because of its mechanical stability and the possibility of welding, stainless steel is good candidate as substrate material. It can be used for cushion absorbers for domestic hot water generation, and also for

receiver tubes for applications working with concentrated solar power (CSP) such as power plants for solar thermal electricity generation, co- and tri-generation. Targeting stainless steel substrates, we focus in this work on the development of multilayered sol-gel coatings for solar absorbers consisting of mixed copper, cobalt, manganese and silicon oxides (Cu-Co-Mn-Si-O). Using suitable multilayer designs, we aim for a solar absorptance above 0.94 and a thermal emissivity below 0.16. Transmission Electron Microscopy (TEM) is used to visualize the microstructure and evaluate the film thickness. Time-of-Flight-Secondary-Ion-Mass-Spectroscopy (ToF-SIMS) and X-Ray Photoelectron spectroscopy (XPS) are employed to determine atomic distribution and their chemical correlation in a triple layered coating on a stainless steel substrate. The coatings shall be deposited with satisfactory homogeneity on stainless steel sheets as well as on collector-sized tubes.

Nomenclature

λ	Wavelength
α_{sol}	Solar absorptance
ε_{th}	Thermal emittance at 100°C
SS	Stainless Steel

2. Methods

2.1. Sample preparation

At the first stage of development, polished sheets of austenitic stainless steel 1.4301 were used as substrate. Their typical size was 7x6 cm^2. These dimensions allow to measure the thermal emissivity of coated substrates by means of the TIR-100 type emissiometer. Substrate roughness was characterized using atomic force microscopy (AFM, Solver Pro-M from NT-MDT) measurements, yielding a root mean square roughness value of 28 nm on a 36x36μm^2 area. Before deposition, the substrate was cleaned in an ethanol bath and placed in demineralized water at 75°C. At the second development stage, the process was adapted to coat austenitic stainless steel tubes with a diameter of 40 mm. For characterization techniques such as spectroscopic ellipsometry or electron microscopy, crystalline silicon wafers were used as well-defined substrates.

The studied materials were composed of copper, cobalt, manganese and silicon (Cu-Co-Mn-Si). The three relative molar ratios in the precursor solutions (at%Cu / at%Co : at%Co / at%Co : at%Mn / at%Co : at%Si / at%Co) were adapted from formulations in other studies [8, 12] and are equal to (3:1:3:0), (3:1:3:1) and (0:0:0:1). However, unlike the studies cited above, silicon was added to the solution in order to produce novel phases and explore their optical and chemical properties.

The Cu-Co-Mn solution (3:1:3:0) was made from manganese (II) acetate tetrahydrate >99% (Acros), copper (II) chloride dihydrate 99% (Acros) and cobalt (II) chloride hexahydrate 98% (Acros). Manganese acetate was first dissolved in nitric acid (HNO_3). Absolute ethanol, cobalt chloride, copper chloride and demineralized water were added stepwise to the solution. By means of a rotary evaporator (Büchi Rotavapor R-210), more than 95 wt% of the ethanol was evaporated (70°C, 108 rpm, 200 mbar) to increase the molar concentration of the precursors. Fresh absolute ethanol was added to the thus obtained solution to reach the initial molar concentration. This step was repeated twice to improve hydrolysis and

condensation reactions in the solution [13]. Finally a surfactant (Triton-X100) was added to the solution and maintained 15 hours at 70°C and ready for the dip-coating deposition.

The solution with a relative molar ratio of (0:0:0:1), based on tetraethyl orthosilicate 98% (TEOS, Acros), was prepared separately. Added to absolute ethanol, TEOS was hydrolyzed in presence of nitric acid and demineralized water. After 15 hours at 50°C, the solution was ready for dip-coating.

The solution with a relative molar ratio of (3:1:3:1) was a mixture of the two previously described solutions. The relative quantities of the (3:1:3:0) and (0:0:0:1) solutions were chosen to obtain a molar ratio Co:Si of 1:1. Once mixed, the obtained solution can be deposited by dip-coating with no further processing.

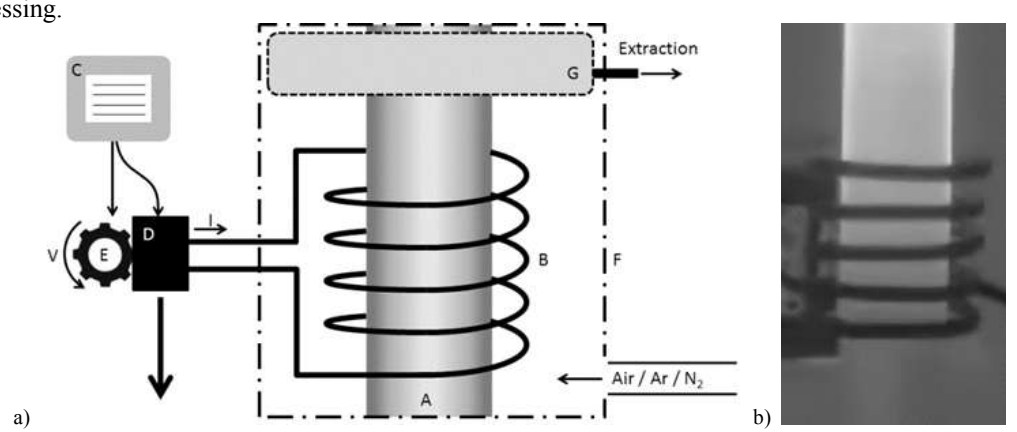

Fig. 1a. Schematic representation of the device used for thermal annealing of the coating by induction heating. Austenitic stainless steel tube (A); induction coil (B); control unit (C); AC generator (D); motor (E) rotating at speed V; coil and tube are surrounded by a chamber (F); gasses emitted during thermal annealing are extracted through an exhaust pipe (G). Fig. 1b. Infrared imaging of the tube during thermal annealing.

The sol-gel solutions described above were deposited using a dip-coating process. This technique allows to produce coatings even in ambient air at a standard room temperature. The dip-coating process comprises three main steps: (1) dipping of the substrate in the solution, (2) withdrawal at constant speed with formation of a liquid film at the surface, (3) evaporation of the solvent and formation of a xerogel [13]. By thermal annealing between 400°C and 500°C in ambient air for a duration of 90 minutes, the films coated on flat substrate were hardened and oxidized in a Vulcan® benchtop furnace (320x360x250 mm^3). With this technique, one can accurately and reliably control the layer thickness as a function of the withdrawal speed and the sol-gel solution viscosity.

While the sheetlike substrates were annealed in a conventional furnace, a novel, fast and energy-efficient process based on induction heating was developed for the thermal annealing of the 2 meter long austenitic stainless steel tubes [14]. The coated tube was passed through a water-cooled induction coil as described in Fig 1a. An alternative (AC) current oscillating in the induction coil at frequencies between 20 kHz and 200 kHz induces a strong AC current in the steel tube, the latter heating up resistively the tubular substrate as well as the film deposited on it. Using this process, the tube and coating reached approximately 400°C within a few seconds, which allows a continuous calcination speed of 1 meter per 5 minutes. After a single passage of the induction coil, the radial and longitudinal distribution of the substrate's temperature was sufficiently homogenous as shown by infrared imaging (Fig 1b).

2.2. Optical characterization

Near-normal spectrophotometric reflectance measurements (380 nm – 2500 nm) were performed on the samples produced. Using an Oriel MultiSpec 125TM 1/8m spectrograph with Instaspec IITM

Photodiode Array Detector and an Optronic Laboratories Monochromator OL 750-M-S coupled to a NIR-sensitive PbS detector (OL 730), solar absorptance, α_{sol}, of the coatings was determined. Additionally their thermal emittance at 100°C, ε_{th}, was measured with an Inglas TIR100 emissiometer.

2.3. Corrosion durability

In order to roughly estimate the corrosion resistance of the coating in an acidic environment, a fast time-response corrosion test in harsh conditions was designed. Two kinds of layers are tested together: a highly durable selective black chrome coating for flat plate collectors available on the market today, chosen as reference, and a selective black coating made according to the sol-gel method in the laboratory. A drop of hydrochloric acid 25 wt% was deposited on both samples and the degradation times were monitored. A digital camera, placed above tested samples, was used to record and compare degradation behaviors. Just after the deposition of the droplet, both coatings are intact, the samples remaining black; the coating is then completely destroyed, when the white color of the stainless steel substrate becomes visible. The test conditions are far from reality and results have to be taken as an indication.

2.4. Microstructural characterization

Structural analysis of different phases were performed by TEM (Philips CM20) and high resolution transmission electron microscopy (HRTEM Philips CM300). Bright field images were obtained from cleaved edge single layers deposited on silicon. These images made it possible to measure thicknesses and obtain morphological information from the deposited films.

2.5. Elemental composition

In order to know the elemental composition of a multilayered coating on a stainless steel (1.4301) substrate, ToF-SIMS and XPS were performed. The multilayered coating is composed of three layers of Cu-Co-Mn-Si oxides with following relative ratios: SS // (3:1:3:0) // (3:1:3:1) // (0:0:0:1) // air. The layers were deposited successively by sol-gel dip-coating.

ToF-SIMS depth profiling was carried out by means of an IONTOF from the top-layer down to the substrate. For film ablation by sputtering, O^{2+} ions (1 keV, 300x300 μm²) were used, whereas Bi^{3+} ions (25 keV, 75x75 μm²) were used for analysis. The cross section measurement makes it possible to visualize the atomic intensity throughout the thickness of the coating. Since reliable quantitative results cannot be obtained by this technique, complementary XPS measurements were performed.

For XPS measurements, a two-chamber ultra-high vacuum (UHV) setup was used. In the preparation chamber, an argon Penning ion source allows the gradual ablation of the coating. This chamber is linked to an electron spectrometer equipped with a hemispherical analyzer (Leybold EA11/100 MCD) and an X-ray source for core level spectroscopy (Mg-Kα excitation, hν = 1253.5eV). As reference, the Au 4f7/2 core level signal at 83.8 eV binding energy was measured from a gold bulk element (999.9 purity). The concentrations of elements were obtained by integrating over the core level signal after subtracting a Shirley background. From the photoionization cross-sections given by Scofield [15], the atomic concentrations were calculated.

3. Results

3.1. Optical optimization

Single layers of Cu-Co-Mn-Si-O with a relative atomic ratio of (3:1:3:0) were deposited on stainless steel substrate. The solar absorptance of the sample was optimized by varying the withdrawal speed. A solar absorptance of 0.86 ± 0.01 was reached for a thermal emissivity of 0.11 ± 0.01, which is fully appropriate for a single layer coating.

The next step consisted in optimizing the solar absorptance of the coating by adding an anti-reflection layer on top of it. The anti-reflection layer used is made of silicon oxide SiO_x (0:0:0:1). The real part of its refractive index was found to be equal to 1.46 for λ=550 nm; this value falls between the refractive

index of air (n=1) and the considered absorbent oxide Cu-Co-Mn-Si (3:1:3:0) (n=1.9). For this double layer configuration, the thickness optimization for individual layers leads to a solar absorptance of 0.94 ± 0.01 for a thermal emissivity of 0.11 ± 0.01.

Optical characterization of the coated samples is shown in Fig. 3. The spectral reflectivity is represented as a function of wavelength for a single layer coating (dotted line I) and a double layer coating (dotted line II) on a stainless steel substrate. The same graph also shows the spectral distribution of solar radiation for comparison purposes.

A graded index coating composed of three distinct layers was then designed. The intermediate layer is a mixture of the bottom (3:1:3:0) and the top layer (0:0:0:1). The real part of its refractive index was found to be equal to 1.6 for λ=550 nm. As an intermediate layer favors the light penetration and absorption, it increases the solar absorption of the coating up to 0.96 ± 0.01 with an emissivity of 0.12 ± 0.01.The monitored spectral reflectivity of this sample is also presented on Fig. 2 (solid line III).

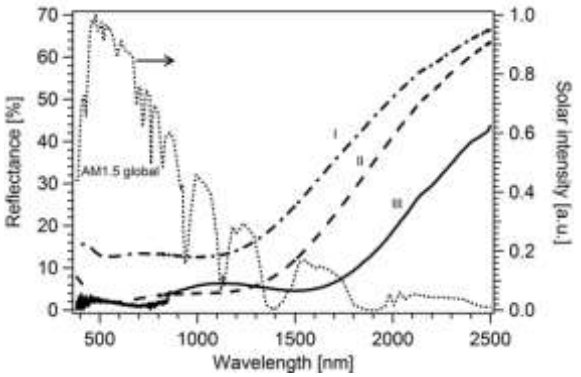

Fig. 2. Spectral reflectivity of black selective samples. The dotted line I represents the reflectivity of a single layer coating (SS // Cu-Co-Mn-O) the dotted line II represents the reflectivity of a double layer coating, (SS // Cu-Co-Mn-O // Si-O) and the solid line III represents the reflectivity of a triple layer coating on stainless steel (SS // Cu-Co-Mn-O // Cu-Co-Mn-Si-O // Si-O). The respective solar absorptions are α_{sol}=0.86 for I, α_{sol}=0.94 for II and α_{sol}=0.96 for III.

.2. Corrosion durability

A simple corrosion resistance test gave an idea of the durability of the novel sol-gel coating in an acidic environment. Fig. 3 shows images of drops of concentrated acid on the samples. The time step between each picture, extracted from the movie, is 20 seconds.

For the reference black chrome coating, the stainless steel substrate can be seen after less than 40 seconds: in the third picture of A series, a marked variation of color is observed, reflecting a sharp deterioration of the coating. The sample produced in the laboratory with the sol-gel triple layer coating shows a complete degradation after three minutes instead of less than 40 seconds. These results suggest that the novel coating might be more durable in acidic environments than the conventional black chrome coating for unglazed flat plate collectors.

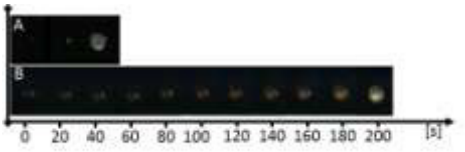

Fig. 3 : Images of black selective coatings during the corrosion test. The A series represents the behavior of a conventional chromium coating; the B series reflects the behavior of the novel coating produced in our laboratory.

.3. Microstructural analysis

In order to study the microstructure of single layers, the Cu-Co-Mn-Si phases were analyzed by TEM. The figure 4 represents a cross-section of a Cu-Co-Mn-Si material with a theoretical relative atomic ratios of (3:1:3:1) deposited on silicon wafer. The latter is easily recognizable with striped dark and light lines. The deposited single oxide layer is observable and the measured thickness between the black and the white arrows is approximately 110nm. The studied (3:1:3:1) Cu-Co-Mn-Si material seems to be composed of an agglomeration of nanocrystalline grains of 5-20nm in diameter. These findings were confirmed by HRTEM (not shown here).

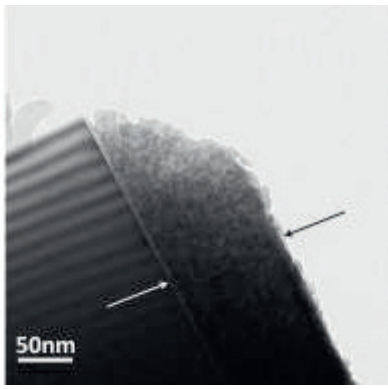

Fig. 4a. Nanocrystalline structure of Cu-Co-Mn-Si-O (3:1:3:1) layer by TEM (bright-field mode).

3.4. ToF-SIMS characterization

In order to obtain black selective surfaces for solar thermal collectors, a novel multilayered coating has been developed. The coating is composed of three thin layers deposited on stainless steel substrate: SS // $Cu_3CoMn_3O_x$ // $Cu_3CoMn_3SiO_x$ // SiO_x. The following paragraphs contain the measurements performed in order to characterize the elemental composition of coatings by ToF-SIMS.

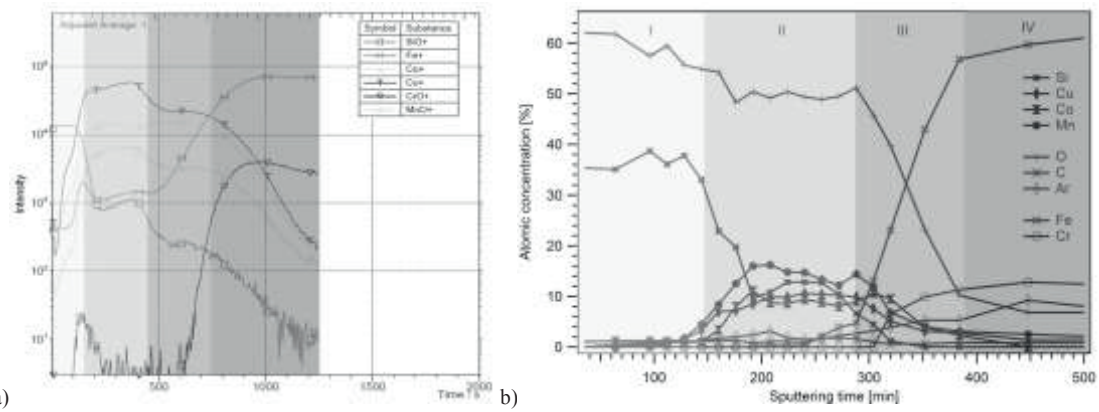

Fig. 5. Depth profile of Cu-Co-Mn-Si triple-layer coating on stainless steel substrate by a) ToF-SIMS and b) XPS.

The depth profile is shown in figure 5a. The element specific detection of copper (Cu), cobalt (Co), manganese (Mn), silicon (Si), chromium (Cr) and iron (Fe) allows the visualization of a stratified coating on stainless steel substrate which confirms the presence of three distinct and superposed layers. Next to the substrate (750s-1250s), the first layer (450s-750s) contains cobalt atoms but very few silicon atoms corresponding to the (3:1:3:0) film. The second layer (150s-450s) contains clearly a mixture of cobalt and silicon corresponding to the (3:1:3:1) film. In this intermediate layer, the concentration of silicon does not seem constant but decreases in direction of the top layer. This upper layer (0s-150s) correspond obviously to the (0:0:0:1) film which encapsulates and protects the whole coating. Unfortunately atomic concentrations were not determined by this method as quantitative measurements were not possible.

3.5. XPS characterization

The depth profile of a triple-layered coating on stainless steel substrate was also characterized by X-ray photoelectron spectroscopy (XPS), yielding the atomic concentration of each element in function of the sputtering time. The atomic concentrations of elements are represented in the figure 5b as a function of sputtering time. Four distinct areas corresponding to the three layers of the coating and the substrate can be recognized. Area I corresponds to the SiOx encapsulating layer with a relative atomic ratio Cu-Co-Mn-Si of (0:0:0:1). In area II, copper, cobalt and manganese appear and silicon is still present. The associated Cu-Co-Mn-Si material corresponds to the concentration ratio (3:1:3:1). In the third area, being associated with the (3:1:3:0) material, atomic concentration of silicon falls to negligible level while atomic concentrations ratios of copper, cobalt and manganese are maintaining. In this area iron, chromium and nickel are already detected due to the roughness of the substrate. Finally, area IV corresponds to the stainless steel substrate with the stabilization of the atomic concentration of oxygen.

It is also interesting to consider the atomic concentration of carbon, represented in figure 5b. Even though deposition by sol-gel dip-coating is based on organic precursors, the carbon atomic concentration remains less than 2 at% throughout the sample. This confirms the near-complete removal of carbon during the thermal annealing. On the contrary, the atomic concentration of argon tends to increase with sputtering time, as is expected when using an argon Penning ion source for ablation: argon atoms are incorporated in the material studied.

3.6. Black selective tubes

The promising stability at 360°C in ambient air [16] makes this three-layer coating an interesting candidate for solar applications involving concentrated solar radiation [17], such as the generation of solar electricity (concentrated solar power), industrial process heating and solar cooling. For that reason, prototype coatings consisting of stacks of three individual layers were deposited on 2 meter long stainless steel tubes. Because identical solutions are used for coatings of sheets and the tubes, their chemical compositions remain similar. However, the new production process which is adapted to the cylindrical geometry of the metallic tubes might result in a slightly different phase composition. For the multilayers obtained by this process, no visible cracks are observed. In addition to that, debonding or peeling effects do not occur, indicating that good adhesion of the individual layers to the substrate and to each other is achieved.

The order of magnitude of the production cost per meter of such black selective tubes was estimated for fabrication made under laboratory conditions. The stainless steel substrate itself costs around 12€/m. The summation of the cost of the precursors and the electrical consumed energy for the solution preparation, film deposition and thermal annealing, was 0.34€/m. As the production process is far from being optimized at this stage, it is difficult to estimate the final operation cost due to the involved manpower. The latter will also depends strongly on the degree of automation.

The highly reproducible homogeneity of the multilayered coatings on 2 meter long stainless steel tubes is illustrated in Fig. 6. The promising results obtained by the novel processing technique demonstrate the commercial potential for sol-gel stacks in concentrated solar power applications.

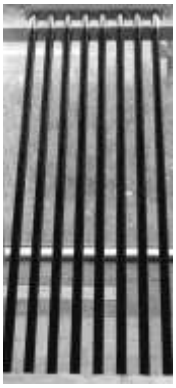

Fig. 6. Two meter long black selective tubes produced in our lab using the novel selective coatings applied using the novel deposition-induction process.

4. Discussion

Multilayered thin films were designed with the aid of computer simulations based on the method of characteristic matrices. While the method is very accurate for optically flat surfaces, it yields only approximate results for rough surfaces. The mathematical treatment of optical properties of rough surfaces is generally a difficult task. However, in this case, the calculation method applicable to flat surfaces and interfaces yields results which can support and direct an empirical optimization of the multilayered design. This is quite remarkable as the RMS roughness of the substrate is of the order of 30nm and the typical thickness of each individual layer is approximately 50-100nm. Moreover, after deposition of the triple layer by sol-gel method, the surface roughness is slightly decreasing.

The top-layer used as a corrosion barrier is made of quartz. The challenge was to make this layer very homogeneous with as little porosity as possible. Moreover, controlling the roughness of layers deposited by a wet chemical process was crucial. All these parameters have been mastered to finally produce a coating as resistant to hydrochloric acid as black chrome coating.

Initially this work was motivated by an application as black selective coating for flat plate collectors. At this stage of the development, it is not yet quite clear whether this process is commercially attractive for this application. However, during our work, we became aware of the fact that the coatings might be especially well suited for the application as black selective tubes. For CSP application, less surface area is coated, therefore the added value through a graded selective coating is large. Moreover, black selective tubes are easier to produce because of the cylindrical geometry and the developed deposition process which make sol-gel coatings especially suitable for the production of selective absorber tubes. Such a high tech component might be competitive with existing commercial options currently used for concentrated solar power plants. First corrosion and thermal resistance tests show a coating with

promising durability. Nevertheless, if further steps forwards an industrialization will be undertaken, the IEA Task 10 procedure [18] still has to be performed.

5. Conclusion

This study describes the development of a black selective coating made by sol-gel dip-coating. The optimization of the optical properties led to a solar absorption larger than 0.95 with a thermal emittance close to 0.12. The multilayered thin films were designed with the aid of computer simulations based on the method of characteristic matrices.

Depth profiles of the multilayered coating by means of ToF SIMS and XPS confirm the presence of three areas with specific chemical composition. TEM images allowed the observation of nanocrystalline particles of 5-20nm in diameter.

Thermal stability and corrosion resistance of novel coatings were compared with those of black chrome coatings, revealing promising properties.

The multilayered black selective coatings were deposited with satisfactory homogeneity on 2 meter long stainless steel tubes. Fast and energy-efficient induction heating was used for thermal annealing.

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